The performance of electrodes in direct-utilization, solid oxide fuel cells (SOFCs) has been studied on anode-supported and electrolyte-supported cells using impedance spectroscopy, coupled with calculations of the potential distribution in the electrolyte. The cells in these studies were composed of a Cu-ceria-yttria-stabilized zirconia (YSZ) anode, a YSZ electrolyte, and a Sr-doped LaMnO$_3$ (LSM)-YSZ cathode and were operated at 983 K using both H$_2$ and n-butane as fuel. Both calculations and experiments show that the spectra associated with anode and cathode measurements can be used to estimate the performance of individual electrodes. Results from these measurements are compared to those obtained using three-electrode measurements and are also compared to those obtained using two-electrode measurements.

Impedance spectroscopy measurements were performed on cells having a Cu-ceria-YSZ anode, a YSZ electrolyte, and a Sr-doped LaMnO$_3$ (LSM)-YSZ cathode. In agreement with other studies, we find that the measured area-specific resistance (ASR) for both anode and cathode depend strongly on the relative placement of the electrodes, cathode, and reference electrode. Fortunately, in our system, impedance spectra indicate that the frequencies associated with anode and cathode processes are widely separated, so that errors caused by interference of kinetics from one electrode on the other can be easily identified. A reasonable separation of electrode kinetics can be achieved by accurate alignment of anode and cathode. The impedance spectra indicate that the differences observed between two-electrode and three-electrode measurements are large, and that the anode performance is strongly dependent on anode and cathode processes are widely separated, so that errors caused by interference of kinetics from one electrode on the other can be easily identified. A reasonable separation of electrode kinetics can be achieved by accurate alignment of anode and cathode.

Here, we have performed an experimental and theoretical study aimed at characterizing SOFC performance on cells having a Cu-ceria-YSZ anode, a YSZ electrolyte, and a Sr-doped LaMnO$_3$ (LSM)-YSZ cathode. In agreement with other studies, we find that the measured area-specific resistance (ASR) for both anode and cathode depend strongly on the relative placement of the anode, cathode, and reference electrode. Fortunately, in our system, impedance spectra indicate that the frequencies associated with anode and cathode processes are widely separated, so that errors caused by interference of kinetics from one electrode on the other can be easily identified. A reasonable separation of electrode kinetics can be achieved by accurate alignment of anode and cathode.

**Methods**

Because oxides of Cu melt at temperatures below than that required for sintering of YSZ, the fabrication of Cu-cermet andes involved preparing a porous matrix of YSZ, impregnating this porous matrix with a Cu salt, and finally reducing the salt to metallic Cu, as described in other publications. In the first step, the porous YSZ matrix was prepared by tape-casting methods, using graphite and poly(methyl methacrylate) (PMMA) pore formers. Firing this tape to 1800 K resulted in YSZ that was ~70% porous, as determined by water-uptake measurements. After attaching the cathode, Cu and ceria were added to the porous YSZ matrix, separately, by impregnation with aqueous solutions of Cu(NO$_3$)$_2$·6H$_2$O and Cu(NO$_3$)$_2$·3H$_2$O, followed by calcination to 723 K in air to decompose the nitrates. The final composition of the anodes used in this study was 20 wt % Cu and 10 wt % CeO$_2$. The anode thickness, equal to the thickness of the YSZ matrix, was 600 μm for all cells in this study.

Three anode-supported cells, having electrolyte thickness of 100, 200, or 350 μm, were prepared. For these cells, the green tape with pore formers was cast over tapes without pore formers, resulting in a tape with two layers. After calcining the two-layer tape to 1800 K, a 50:50 mixture of YSZ and LSM (La$_{0.6}$Sr$_{0.4}$MnO$_3$), Praxair Surface Technologies) powders was applied as a paste onto the dense side of the wafer, after which the sample was calcined to 1400 K to form the cathode. To determine the effective cathode size on the impedance measurements, the 100 and 200 μm cells had semicircular cathodes with an area of 0.16 cm$^2$, while the 350 μm cell had a circular cathode, 0.32 cm$^2$. On the cell with a 200 μm electrolyte, an
LSM-YSZ reference electrode, with an area less than 0.02 cm$^2$, was attached on the cathode side at distance from the cathode that was well over three times the electrolyte thickness, as shown in Fig. 1a.

For the electrolyte-supported cell, a thicker green tape, one that led to a dense YSZ wafer that was 550 μm thick, was prepared. A circular piece of a tape with pore formers was laminated onto the electrolyte tape, after which the laminated tapes were calcined to 1800 K. The cathode on this cell was applied using a template that exactly matched the size of the anode and the template was positioned in exact alignment with the anode by placing the cell on a light box. The reference electrode was again made from LSM-YSZ and was attached on the cathode side at distance from the cathode that was well over three times the electrolyte thickness, as shown in Fig. 1b.

Electronic contacts were formed using Pt mesh and Pt paste at the cathode and reference electrodes and Au wire and Au paste at the anode. The cells were sealed onto 1.0 cm, alumina tubes for the anode-supported cells and a 2.0 cm tube for the electrolyte-supported cell using a zirconia-based adhesive (Aremco, Ultra-Temp 552-VFG). Pt lead wires were connected to the Pt and Au current collectors, after which the entire cell was placed inside a furnace and heated to 983 K at 2 K/min in flowing $\text{H}_2$. $\text{H}_2$ and $n$-butane were fed directly to the anode without reforming, as discussed elsewhere. Before making measurements in hydrogen, the anode was exposed to $n$-butane fuel for 20 min to activate the cell, as discussed elsewhere. Fuel flow rates were maintained at approximately 1 cm$^3$/s, ensuring that fuel conversion was always below 2% for $\text{H}_2$ and even lower for $n$-butane.

Half-cell measurements were also performed on a 600 μm, YSZ electrolyte wafer that had LSM-YSZ electrodes and LSM-YSZ reference electrodes attached on both sides. Care was again taken to align the 0.6 cm electrodes on opposite sides of the electrolyte at the center of the disk, as shown in the diagram in Fig. 1b. Pt current collectors and lead wires were attached to all three electrodes and the sample was then heated to 983 K at 2 K/min inside a furnace. All impedance data were recorded in the galvanostatic mode, with most data taken at a dc current density of 350 mA/cm$^2$, using a Gamry Instruments, model PC4 potentiostat. The ohmic resistance of the Pt lead wires at 983 K was measured and subtracted from the data. The total cell impedance curves were measured using a two-electrode method in which the cathode acted as the working electrode and the anode as the counter and reference electrode. Cathode impedance results were recorded using a three-electrode technique with the cathode as the working electrode, the reference electrode as the reference, and the anode as the counter electrode. Anode results were recorded using the same reference electrode, with the counter and working electrodes reversed.

To determine the effect of cell geometry on our experimental, three-electrode system, we performed calculations using the methods described by Adler. In these calculations, the cell is represented by the simple circuit shown in Fig. 2a. Each electrode in this model is described by an R-C circuit, while the electrolyte is viewed as being a simple resistor. Although the impedance spectra for SOFC electrodes often contain several arcs associated with various physical processes, we have chosen to model only the dominant processes observed in our system. The primary aim of the calculations presented here was to examine the impact of test geometry on our ability to separate responses from the two electrodes, not to provide an exact fit to the spectra.

Following the work of Adler, the electrical circuit representing the fuel cell was transposed to a two-dimensional model, as shown in Fig. 2b. The potential distribution through the cell was calculated as a function of position and time for a sinusoidal perturbation of the system with varying frequency, using the Laplace equation to determine the potential distribution in the electrolyte. The electrodes are represented as boundary conditions, $B_A$ and $B_C$, on either side of the electrolyte. These electrode boundary conditions define the current at the electrode-electrolyte interface in terms of the electrode resistance, $R_A$ or $R_C$, electrode capacitance, $C_A$ or $C_C$, and the electrode potential. This approach allowed us to investigate the effect of electrode size and position on three-electrode measurements. All other surfaces were set with insulating boundary conditions to represent the inert electrolyte surface in our experimental geometry.

In the calculations, the reference potential was taken as the surface potential of the electrolyte on the cathode side, sampled three electrolyte thicknesses distant from the cathode. (For theoretical comparisons, we also calculated electrode impedances for a reference that was physically at the center of the electrolyte and for a floating reference, whose physical position moved with frequency so as to remain at the center of the potential distribution.) The impedance of the individual electrodes was then given as the ratio of the potential difference between the electrode and the reference potential to the cell current density. The total, two-electrode impedance was taken as the ratio of the potential difference between the two electrodes and the cell current density. As expected, the total impedance was equal to the linear summation of the individual electrode impedances. Obviously, the impedance spectra were determined by calculating the impedances as a function of frequency.

In the calculations, the cathode resistance, $R_C$, capacitance, $C_C$, and resistance, $R_E$, were set to ensure a characteristic frequency of 2 kHz and a resistance of 0.4 Ω cm$^2$, while the anode parameters were chosen to provide a characteristic frequency of 4 Hz and a resistance of 0.8 Ω cm$^2$. These values were chosen to match the dominant processes that were determined experimentally on our cells, operating at 983 K in $\text{H}_2$. In the calculations, the potentials of the cathode and anode were fixed at 200 and −200 mV. The system of equations was solved...
using a triangular mesh, finite-element method, using MATLAB 6.5 (The Mathworks, Inc.) on an 866 MHz Intel Pentium III PC. The mesh size was chosen to ensure that the calculated impedance curves were independent of the mesh geometry.

Results

The results obtained on the anode-supported cells are described first, because they demonstrate that the electrode impedance curves are highly reproducible and that the measured ASR are independent of the electrolyte thickness or cathode area. Figure 3 is a Cole-Cole plot of the two-electrode impedance results for anode-supported cells having an electrolyte thickness of 100, 200, and 350 μm, normalized to the area of the cathodes. The frequency-dependent arcs in each curve are due to the two electrodes; and the sum of the electrode resistances, $R_E$, is the difference between the high-frequency and low-frequency intercepts with the real-axis. The high-frequency intercept with the real-axis gives the purely ohmic losses in the cell, $R_V$, which are caused primarily by the electrolyte.

Several important observations should be noted from the data in Fig. 3. First, since the cathode area for the 350 μm cell was different from the other two, the results are independent of cathode area when properly normalized, as others have already pointed out. This allows us to compare data from an anode-supported cell to that from an electrolyte-supported cell so long as the results are normalized to the cathode area. Second, the ohmic resistances in these three cells were 0.71, 1.06, and 1.78 Ω cm$^2$. If one uses the literature value of 0.021 S/cm as the conductivity of YSZ at 983 K, the calculated ohmic resistances should all be lower by 0.23 Ω cm$^2$. Assuming that 0.23 Ω cm$^2$ is due to contact resistance with the current collectors, the rest of the ohmic losses scale linearly with the thickness of the electrolyte. Third, ohmic losses are dominated by two processes with characteristic frequencies at 4 Hz and 2 kHz. While a perfect fit of the two-electrode spectrum would require a third process at an intermediate frequency, the 4 Hz and 2 kHz processes clearly dominate the spectrum.

Finally, based on the data in Fig. 3, the two-electrode impedances were essentially independent of dc bias for operation in H$_2$ at 983 K. The total electrode resistances, $R_E$, for the anode-supported cells were 1.31, 1.33, and 1.34 Ω cm$^2$ for the 100, 200, and 350 μm cells, respectively. These three values are within experimental error of each other, even though the dc potentials on the three cells had to be changed to maintain the current density at 350 mA/cm$^2$.

For operation in H$_2$ at 983 K, the total electrode resistance was also independent of current density, as demonstrated by the data in Fig. 4 and 5. In Fig. 4, the V-I curve for H$_2$ on an electrolyte-supported cell with a 550 μm electrolyte, is essentially linear for current densities ranging from 0 to 400 mA/cm$^2$. Since the slope is equal to the total cell resistance and $R_{Ω}$ must be constant, $R_E$ must
also be constant. This independence of the current density is also shown in Fig. 5, where the two-electrode impedance spectra for the same cell as in Fig. 4 are shown at several current densities. The total cell resistance in Fig. 5, 4 Ω cm², is also in good agreement with the slope of the V-I curve in Fig. 4.

However, the cell resistance for operation in n-butane is a function current density, as shown by the changing slope of the V-I curve in Fig. 4 and the two-electrode impedance spectra in Fig. 6. Figure 6 reports the impedance spectra measured at 50, 100, 200, and 400 mA/cm² and indicates that total cell resistance decreases from 7.8 to 3.3 Ω cm² as the current density increases. There are also two dominant arcs in the impedance spectra of Fig. 6. The first of these has a characteristic frequency of 2 kHz, spans 0.4 Ω cm², and is independent of current density. That there is a similar arc in the spectra for H₂ suggests that it should be attributed to cathode processes, an assignment that is confirmed by the three-electrode measurements to be discussed later. The second arc has characteristic frequencies and resistances that depend on the current density for n-butane. Again, by comparison to the spectra for H₂ in Fig. 4, this low-frequency region can be attributed to anode processes. It is noteworthy that the characteristic frequencies and resistances for the low-frequency arcs are similar for both n-butane and H₂ at higher current densities, suggesting that there is an activation polarization for n-butane that, once overcome, allows the performance curves for the two fuels to be similar. As expected, the ohmic resistance, RΩ, attributed to the YSZ electrolyte, is independent of fuel.

Three-electrode impedance spectra were measured on an anode-supported cell in an attempt to confirm the tentative assignments given above; however, the experimental and theoretical results shown in Fig. 7 demonstrate that the reference electrode on an anode-supported cell provides no additional information. The experimental data at the top of Fig. 7 were obtained using the three-electrode method on the 200 μm cell, with the placement of the reference electrode as shown in Fig. 1a. Based on this data, the anode resistance, Rₐ, is only 10 mΩ cm², while the cathode resistance, Rₓ, is 1.31 Ω cm², the same value as the total of the electrode resistances measured using the two-electrode method. Furthermore, the assignment of the total cell impedance spectrum to the cathode is in direct conflict with our observations of the changing nature of the spectra with fuel. Finally, 97% of the ohmic resistance appears in the cathode spectrum, indicating that potential of the reference electrode is close to that of the anode, even though the reference electrode is on the cathode side. As others have pointed out, it would be incorrect to calculate resistances for either the anode or cathode from this data.

The calculated impedance curves at the bottom of Fig. 7 help to explain the measurements on the anode-supported cell. For this calculation, we assumed that the anode has a resistance, Rₐ, of 0.8 Ω cm² and a characteristic frequency of 4 Hz, while the cathode is described as having a resistance, Rₓ, of 0.4 Ω cm² and a characteristic frequency of 2 kHz. The calculated impedance curves match the experimental data reasonably well. Figure 8, which shows the calculated potential distribution at 100 MHz, demonstrates the reason for this. Here, equipotential lines are shown to extend from the anode surface to the exposed electrolyte at the cathode, only a short distance from the edge of the cathode. Therefore, a reference electrode placed on the top surface of the electrolyte is at the same potential as the anode, -200 mV in this case, and the reference electrode and anode are effectively short-circuited. The very low ohmic resistance associated with the anode spectrum in Fig. 7 is a direct result of this fact, as is the fact that the apparent cathode impedance curve is identical to the impedance curve for the sum of the two electrodes. Clearly, one cannot abstract information about either the anode or the cathode from three-electrode measurements using a reference electrode on an electrode-supported cell.

Separation of anode and cathode processes can be accomplished using reference electrodes and cells with a symmetric alignment of the working electrodes. However, it has been shown that even small misalignments in the relative positions of the electrodes and...
differences in characteristic frequencies of the anode and cathode kinetics\(^{22}\) can affect how well one can separate the losses associated with each electrode. Calculations suggest that the ratio of the misalignment between the anode and cathode, \(\delta\), to the electrolyte thickness, \(L\), must be less than 0.5,\(^{14}\) so that proper alignment becomes very difficult if \(\delta\) is too thin. We chose to use 550 \(\mu\)m electrolytes as a compromise, since this is thin enough to allow reasonable current densities at 983 K and thick enough to make electrode alignment possible.

Before discussing the experimental results, it is useful to consider the calculated impedance curves as a function of electrode misalignment for our geometry. As in Fig. 7, we assumed that the anode has a resistance of 0.8 \(\Omega\) \(\mathrm{cm}^2\) and a characteristic frequency of 4 Hz and that the cathode is described as having a resistance of 0.4 \(\Omega\) \(\mathrm{cm}^2\) and a characteristic frequency of 2 kHz. The calculations were similar to those reported by Adler,\(^{22}\) with the calculated impedance curves shown in Fig. 9 for \(\delta/L\) equals 2, 1, and 0.5. For these calculations, the reference potential was chosen to be the potential of the electrolyte surface on the cathode side, more than 3\(L\) from the cathode, and the anode is assumed larger than the cathode, making it extend beyond the cathode.

For \(\delta/L\) equals 2 in Fig. 9a, the reference potential at high frequency is equal to the potential between the working electrodes at a position 0.13\(L\) from the anode, as demonstrated by the ohmic resistance of the arc at the left being 13% of the total ohmic resistance. However, even though the reference potential is equal to a potential within the electrolyte at high frequency, the calculated \(R_o\) from the anode arc in Fig. 9a is 0.51 \(\Omega\) \(\mathrm{cm}^2\), significantly less than the actual value used in the calculation of 0.80 \(\Omega\) \(\mathrm{cm}^2\). The remainder of the anode resistance appears as a 4 Hz arc in the cathode spectrum, which is now significantly underestimated. The summation of the anode and cathode spectra still yields the correct, total electrode result that would be measured in a two-electrode measurement, showing that this consistency check is not meaningful. Reduction of the anode extension to \(\delta/L\) of 1, Fig. 9b, pushes the high-frequency potential of the reference to a distance 0.27\(L\) from the anode and improves the measured \(R_o\) to a value of 0.77 \(\Omega\) \(\mathrm{cm}^2\), although the cathode resistance, \(R_c\), is now 0.51 \(\Omega\) \(\mathrm{cm}^2\), an overestimate of the actual value by 27%. Finally, further reduction of \(\delta/L\) to 0.5, Fig. 9c, places the high-frequency potential of the reference electrode to a distance 0.38\(L\) from the anode; but both the anode and cathode resistances are determined to be too high by 9 and 35%, respectively.

Even for perfect alignment of the working electrodes, the values for \(R_o\) and \(R_c\) determined from three-electrode measurements may still be inaccurate due to inductance artifacts, first reported by Adler.\(^{22}\) These artifacts were reproduced in Fig. 10 for cathode and anode parameters similar to those in our cells. The calculated spectra in this figure assume perfectly aligned electrodes. It is noteworthy that the values of \(R_o\) and \(R_c\) that would be determined from Fig. 10 are too high by 25 and 12%, respectively. The anode and cathode arcs still sum to the correct two-electrode result, since the inductive artifact in the anode curve cancels the overestimate in the cathode curve and vice versa.

The artifacts in Fig. 10 are caused by the large difference in the characteristic frequencies of the two electrodes, which in turn causes the potential of the reference electrode to move with the frequency of the measurement. This is shown in Fig. 11, where the fraction of the real cell impedance attributed to the cathode is shown as a function of frequency. Two cases are shown: In the first, the reference potential is chosen to be that potential that exists at the physical center of the electrolyte; in the second, the physical position of the reference potential is allowed to move with frequency so that potential is always equal to midpoint of the electrolyte potential drop. This perfect, floating reference is not experimentally feasible but it is useful to consider as a point of comparison.

At high frequency, the electrolyte potential distribution is symmetric and 50% of the real impedance is correctly found in both cathode and anode spectra. As the frequency decreases to the characteristic frequency of the cathode, both the fixed and floating references correctly show an increase in the cathode contribution to the total impedance. However, the fixed reference does not equal the midpoint of the potential drop and overestimates the cathode contribution due to asymmetry in the electrolyte potential distribution.\(^{22}\) The cause of this asymmetry is the difference in characteristic frequencies of the anode and cathode that leads to a phase shift in the potential through the electrolyte. An analogous pattern emerges as

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**Figure 8.** The calculated potential profile at \(1 \times 10^8\) Hz through a 200 \(\mu\)m electrolyte, anode-supported cell.

**Figure 9.** Calculated impedance spectra for a 550 \(\mu\)m electrolyte cell with anode \(\delta/L\) ratios of (a) 2, (b) 1, and (c) 0.5. The spectra shown are two-electrode (▲) Anode → Cathode, (△) Ref. → Cathode, and (○) Ref. → Anode.
the frequency decreases toward the characteristic frequency of the anode. At very low frequency, the fixed reference overestimates the cathode contribution due to a slightly asymmetric potential distribution caused by the relatively large anode resistance. This demonstrates a theoretical limitation to the separation that is obtainable with the three-electrode spectra.

Figure 12 gives the three-electrode impedance curves for the cathode and anode, as well as the two-electrode measurements, on the electrolyte-supported cell, using the configuration shown in Fig. 1b. The high ohmic resistance is due to the relatively thick electrolyte, 550 μm. These measurements were again performed in H₂ at a current density of 350 mA/cm². The ohmic resistance obtained from the two-electrode measurement is essentially identical to that obtained on the anode-supported cell in Fig. 2, providing confidence that the performance of the electrodes on the electrolyte-supported cell is similar. Since 44% of the total ohmic resistance is present in the cathode spectrum, the potential of the reference electrode must be close to the center of the electrolyte at high frequency. Based on calculations like those shown in Fig. 9, we estimate that the misalignment, \( \frac{d}{L} \), of the two electrodes must be significantly less than 0.5.

The data in Fig. 12 provides further evidence that the characteristic frequencies for the anode and cathode are 4 Hz and 2 kHz, respectively, and is in agreement with the observations made from Fig. 5 and 6. The presence of a 4 Hz shoulder on the cathode spectrum, as well as a small 2 kHz arc on the anode spectrum, suggests that we have still not completely separated the anode processes from the cathode; however, a reasonable fit to the anode and cathode results can be obtained by assuming the resistances corresponding to the cathode and anode are approximately 0.4 and 0.8 \( \Omega \cdot \text{cm}^2 \), the same numbers we used in the calculations.

Further evidence that the separation of anode and cathode processes is incomplete in our three-electrode measurements comes from the observation that there are frequency-dependent artifacts in the cathode spectrum which depend on processes occurring at the anode. Figure 13a is the cathode spectrum of the cell used for the data in Fig. 12 when it is operating in H₂, while Fig. 13b is the cathode spectrum measured when the cell is operating in C₄H₁₀, both at the same current density. The ohmic resistance has been subtracted from these curves to aid comparison, although the separation of the ohmic resistance was almost identical for the two fuels, with 44 and 46% of the ohmic resistance present in the cathode spectra for H₂ and C₄H₁₀, respectively. Since the cathode should be dependent only on the current density and independent of processes occurring at the anode in the ideal case, the results in Fig. 13b help confirm our conclusion that features from the anode are exhibited in the cathode spectrum. Since the frequency associated with the anode spectrum for C₄H₁₀ at 350 mA/cm² is also 4 Hz and \( R_\text{A} \) is similar for C₄H₁₀ and H₂ at this current density, evidence for a 4 Hz process is present in both cases. However, apparently because 350 mA/cm² occurs at a different cell potential for C₄H₁₀, the artifact in the
In our attempt to obtain a cathode curve that is free of artifacts from anode kinetics, we performed half-cell measurements on a YSZ wafer with LSM-YSZ electrodes on both sides, with the cathode spectrum shown in Fig. 13c. The sample was held in air at 983 K and a current density of 350 mA/cm² was again imposed across the electrodes. The ohmic resistance ratio on the two electrodes was split 46:54, demonstrating that electrode alignment was acceptable.

While the two electrodes gave essentially identical results, the electrode kinetics for LSM-YSZ under anodic conditions was not identical to the kinetics under cathodic conditions, so that artifacts due to interactions between the electrodes were not eliminated. The 20 Hz feature in Fig. 13c is probably due to anode kinetics, since a significant 20 Hz arc was observed in the anode spectra. However, the main arc in Fig. 13c is clearly a 2 kHz feature with a characteristic resistance between 0.4 and 0.5 Ω cm². Even under these conditions, it was not possible to get a cathode spectrum that was unaffected by anode kinetics.

Discussion

The development of better SOFC anodes and cathodes is obviously aided by our ability to measure the performance of those electrodes, separate from the other components of the cell; and the only way to achieve this measurement is through the use of reference electrodes. While others have already pointed out the importance of having the correct electrode geometry, the experiments and calculations we have reported here demonstrate that it is difficult to separate the performance of one electrode from the other using a geometry that is similar to ordinary planar cells. Certainly, the common practice of using reference electrodes on electrode-supported cells should be stopped because it provides no additional information over that obtained in two-electrode measurements between the working electrodes themselves. The fact that anode and cathode results from three-electrode measurements add up to give the total electrode losses measured in two-electrode measurements is not meaningful, since this observation will hold true even when the data is seriously in error, as our measurements on the anode-supported cells demonstrate.

All difficulties discussed in the present study using impedance spectroscopy are equally important for current-interrupt measurements of electrode overpotentials. Current-interrupt measurements can be thought of as the pulse analogue of a continuous wave spectroscopy; and a Fourier transform of the output from the current interrupt measurements should yield similar information to that obtained in impedance spectroscopy, if the measurement accuracy were sufficient. The advantage to using impedance spectroscopy is that, so long as each electrode has different characteristic frequencies, one can use frequency information to check for signal from one electrode feeding into the other. In the present study, we found this particularly useful in our examination of the cathode, since the characteristic frequencies of the cathode and anode in our cell were quite different.

The calculations and experiments suggest that the fraction of the total ohmic resistance that is given to each working electrode in three-electrode experiments is an important measure of how useful the reference electrode measurements are. Clearly, this parameter should always be reported in three-electrode measurements, since the errors can become significant if the ohmic spli is not close to 50:50. Unfortunately, even when the reference electrodes are placed on electrolyte-supported cells with the working electrodes placed symmetrically, differences in the kinetics of the working electrodes can affect what losses are assigned to each electrode.

It is clear from the comparison of the experimental data to calculations that there is significant uncertainty in the electrode ASR, even for perfectly symmetric electrodes; and low precision may simply be an intrinsic factor in measurements with these types of reference electrodes. We were fortunate that electrodes examined in this work are dominated by single processes, with characteristic frequencies for the anode and cathode separated by three orders of magnitude, so that we could at least determine that there was a problem of...
interactions between the electrodes. Coupled with our ability to run the cells with various fuels, this has allowed us to clearly separate the two processes using a relatively simple cell geometry and electrodes similar to those used in our normal, anode-supported cells. (The use of different fuels, or different fuel compositions, is also feasible with traditional SOFC systems and can provide a useful consistency check.)

As discussed in the Introduction, alternative geometries and electrode placements have been proposed to measure electrode performance.\textsuperscript{20,21} For us, the challenge in using these techniques is in maintaining the fabrication procedures we use to make the anode-supported cells and translating that to the novel electrode geometry required for measuring electrode performance. However, even with such geometries the effect of frequency on the electrolyte potential distribution must be studied, as a reference electrode that measures the potential at the center of the electrolyte is not a guarantee of accuracy.

Obviously, the measurements and calculations shown in this paper confirm the reports of others that the measurement of electrode performance using reference electrodes requires great care.\textsuperscript{13-22} Still, with proper care, the information that these experiments yield can be valuable for optimization of SOFC electrodes.

**Conclusions**

The following conclusions can be reached from this study

1. The measurement of electrode performance using reference electrodes requires cells with a symmetric placement of the working electrodes. No additional information is gained with reference electrodes on anode-supported cells.

2. Separation of anode and cathode processes can be difficult, even in symmetric cells, when the kinetics of the two electrodes are significantly different. Consistency checks are therefore important. One such check is the determination of the fraction of the ohmic resistance between the reference and each electrode. Another check is the determination of cathode performance in different fuels.

3. The ASR for the Cu-ceria-YSZ anode operating in H\textsubscript{2} at 983 K is \(-0.8\ \Omega \ \text{cm}^2\) and independent of current density. The anode exhibits a single characteristic frequency of 4 \text{Hz}.

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